

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :  H05B 33/10		A1	(11) International Publication Number: WO 99/07189  (43) International Publication Date: 11 February 1999 (11.02.99)
(21) International Application Number: PCT/GB98/02211  (22) International Filing Date: 24 July 1998 (24.07.98)		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 9715907.3 29 July 1997 (29.07.97) GB		Published With international search report.	
(71) Applicant (for all designated States except US): CAMBRIDGE CONSULTANTS LIMITED [GB/GB]; Science Park, Milton Road, Cambridge CB4 4DW (GB).			
(72) Inventors; and (75) Inventors/Applicants (for US only): BARNARDO, Christopher, John, Andrew [GB/GB]; Cambridge Consultants Limited, Science Park, Milton Road, Cambridge CB4 4DW (GB). TOWNSEND, Janet, Elizabeth [GB/GB]; Cambridge Consultants Limited, Science Park, Milton Road, Cambridge CB4 4DW (GB). SINGHAL, Kavita [GB/GB]; Cambridge Consultants Limited, Science Park, Milton Road, Cambridge CB4 4DW (GB).			
(54) Title: ELECTROLUMINESCENT DEVICE PRODUCTION PROCESS			
(57) Abstract			
<p>The present invention provides a method of producing an electroluminescent device which comprises the steps of applying a first conductive electrode to a substrate using a standard printing process to apply a Light Emitting Polymer on top of though not necessarily adjacent to said first electrode applying a second conductive electrode on top of though not necessarily adjacent to said Light Emitting Polymer whereby an accurately-placed layer of Light Emitting Polymer of controllable thickness is formed using a method which is as fast and cost-effective as desired.</p>			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Electroluminescent device production processField of the invention

5 The present invention relates to a method for producing electroluminescent devices from Light Emitting Polymers (LEPs) in which a light emitting layer is sandwiched between conducting layers.

10 Background Art

Electroluminescent (EL) devices comprising an active LEP layer sandwiched between conductive layers are known in the art (see, for example WO-A-90 / 13148).

15 WO-A-90 / 13148 discloses a class of Light Emitting Polymers (LEPs) consisting of conjugated polymers such as poly(p-phenylenevinylene) (PPV) and possible substitutes which may, amongst other things, be used for the production of EL  
20 devices. Other LEPs are known which consist of a single material which may be applied to a surface and which can be induced to emit light by the application of a voltage. LEPs have been relatively recently discovered and are treated with a great deal of care by persons skilled in the art - such  
25 treatment involving the use of vacuum cabinets, specialised atmospheres (pure nitrogen etc.) and so on.

Other materials are known which have such light emitting characteristics. These other materials consist of small solid  
30 particles suspended in a binder. Examples of such materials include suspensions of phosphor in a polymer medium chosen for its ease of evaporation or of conversion to form readily a usable, solid, layer of light emitting matter. These suspension materials are more widely known in the art than  
35 LEPs and are perceived as being robust, i.e. these materials do not need the special treatment involved in handling LEPs. Methods for the production of devices using such suspension

materials include the use of single-stage, direct application printing processes such as screen-printing (see, for example, EP-A-0 357 443, US-A-4 614 668, US-A-4 665 342). The general possibility of using roller printing for the printing of such phospher layers was mentioned in passing in EP-A-357 443, although the disclosure of this patent concentrates on the screen-printing of such phosphor layer devices. The suspension substances are subsequently converted to rigid form by heating under controlled environments such as in nitrogen, in a vacuum or by exposing to ultraviolet light.

By contrast, known methods of producing EL devices from LEPs consist of specialised methods such as spin coating, draw coating, melt processing, ion-beam sputtering, radio frequency sputtering, DC sputtering, depositing by evaporation or glow discharge of silane and evaporation of the material onto a substrate (see WO-A-90 / 13148 which extensively describes the various applicable methods for applying LEPs to substrates). These methods are clearly appropriate for a specialised material such as an LEP which needs careful treatment as mentioned above. In order to carry out such application methods, it is desirable that any solvent used with such LEPs is highly volatile and that the mix which is to be deposited should have as low a viscosity as possible. Typically, methanol has been used as a solvent in the prior art.

It is a major disadvantage of these processes that each is only workable for a relatively small surface area.

A further major disadvantage associated with LEPs, at the present time, is that these materials have to be treated with great care and applied to surfaces using complex, expensive, slow processes, as detailed above, which are, in any case, only workable for a relatively small surface area. It is desirable to produce layers of LEP which are thin and uniform - both from the point of view of cost of the material applied and of operational efficiency - and which may be produced over relatively large surface areas in a cost-effective manner. The

screen-printing processes used with suspension materials have not been considered to be suitable for the application of LEPs to substrates, given the care that is involved in handling such materials in the prior art and given the perception that 5 screen-printing would produce a layer that was of the order of 100 times too thick to be of any use.

Another disadvantage associated with LEPs is their short lifetime, making them unsuitable for such applications as 10 cathode ray tube replacements.

Printing processes such as letter-press printing, screen-printing, doctor blade coating, ink-jet printing, roller printing, reverse-roller printing, offset lithographic 15 printing, flexographic printing and web offset printing are known in the art of printing text on paper and various other domains. The use of screen-printing for applying robust, suspension materials in order to create electroluminescent devices is also known in the art, as mentioned above.

20

#### Summary of the Invention

The present invention involves the novel and inventive use of known printing processes in order to apply known LEPs to a 25 substrate.

The prior art clearly leads a person skilled in the art away from the use of printing processes for the application of LEPs to surfaces, as mentioned above. Given this situation, the 30 person skilled in the art would not even consider carrying out experiments to determine whether it were possible to print LEPs using standard printing processes.

Also, the person skilled in the art would not and could not 35 appreciate that the use of, for example, an offset lithographic printing process may be used to apply an LEP to a substrate with the new, surprising effect that such electroluminescent devices work and may be produced in this

way with hitherto unthought of accuracy, in exceptionally thin, uniform layers and using a process which is well-understood, very cheap and very fast.

- 5 Further aspects, advantages and objectives of the invention will become apparent from a consideration of the drawings and the ensuing description, which, by way of example, describe an embodiment of the present invention in which poly(p-phenylenevinylene) (PPVs) are applied to a substrate using
- 10 offset lithographic printing:

#### Brief Description of Drawings

- 15 Figure 1: A schematic representation of the offset lithographic printing process.
- Figure 2: A schematic of an example of a complete LEP sheet structure
- Figure 3: A schematic of a second example of a complete LEP sheet structure

20

#### Detailed description of the invention

The invention is based on the novel and inventive development that some or all the components needed to form an

- 25 electroluminescent device from LEPs can be formed by printing using a standard printing process, such as multiple-stage printing processes like the offset lithographic processes widely used for low cost high volume printing. This method enables large volumes of electroluminescent displays to be
- 30 produced in a much simpler and cost effective manner than has previously been known.

The offset lithographic printing process is a method of depositing inks on a substrate by transferring ink initially

- 35 from a printing plate on to a cylinder covered with a special compressible blanket, which enables a very thin and even coating to be obtained. The offset blanket further splits the

ink film between the printing plate and the blanket which results in a thinner ink film being deposited on a substrate. The printing plate may be patterned to accept or repel the ink by using hydrophilic and hydrophobic regions. The regions which are non-miscible with the ink (i.e. the hydrophobic regions) are deposited at the same time as the ink via damper rollers to wet the plate. Thus, ink adheres only to the appropriately patterned layer and repeats the pattern when transferred to the substrate.

10

The viscosity and volatility of a solvent used for the liquid which is to be printed using the offset lithographic process must be such that not only does it deliver the ink onto the rollers but also such that it is not adversely affected by the printing processes, for example, such that it does not evaporate from the rollers. In direct opposition to the prior art teaching which teaches the use of high volatility, low viscosity solvents such as methanol (as mentioned above), the present inventors have successfully and surprisingly used low volatility, higher viscosity solvents to great effect. Persons skilled in the art would also not have considered the possibility of using such solvents as a transport medium for the particular components to be printed such as the active light emitting layer (e.g. a PPV precursor polymer), conductive polymer and/or barrier materials. A highly polar solvent such as water enables the light emitting layers to be deposited in a pattern using the conventional planographic nature of offset lithographic printing.

20 The evaporation rate and viscosity of the solvent may be controlled by active temperature control of the rollers comprising the printing press. Alternatively the PPV mix, ink ducts or substrates may be preheated. Heating or cooling in this manner also provides additional control over the curing process of components such as that of the PPV precursor polymers.

25

Atmosphere control over the printing press assists in curing of the compounds in question, for example, applying a vacuum or excluding oxygen by applying a nitrogen blanket around the press. Where needed printed sheets may be heated for a period 5 in order to initiate the cure process needed for to convert a PPV precursor polymer.

Figure 1 shows a schematic depiction of the offset lithographic printing process. The offset lithographic process 10 is a method well suited to producing very thin layers of ink. Furthermore, the process achieves substantially higher resolution than other printing processes.

Very thin flat layers of active layer in an EL device are 15 beneficial in that they consume less power. Also, the ability to apply LEPs with very high resolution enables the production of high quality displays of uniform brightness. Depositing multiple layers of the same material or of different materials in sequence enables the complete structure to be built in a 20 controlled manner to give optimum performance.

A solution of precursor PPV in water may be prepared according to standard practices used for creating methanol based 25 solutions (see e.g. J.H.Burroughes et al, Light emitting diodes based on conjugated polymers, Nature vol.347, pp.539-541, October 1990). An aqueous solvent combines the characteristics of a polar solvent, low volatility and adequate solubility for the solution processable PPV precursor. Various concentrations of PPV precursor in solution 30 could be used including completely saturated solutions.

In operation, the solution of PPV precursor is placed in the ink duct [1] and transferred in the standard manner over rollers [2] before forming an even film over the printing 35 plate [3], being transferred to the compressible blanket [4] then transferred to sheets of substrate material [5] passing over the compressible blanket [4]. For patterning, immiscible

liquid [6] may be delivered simultaneously via an set of damper rollers [7].

Sheets of polyester [8] coated with a conducting layer of indium tin oxide (ITO) [9] may be used as a substrate. A uniform layer of LEP [10] is deposited over the complete sheet which could be passed through the print press several times to achieve the desired thickness of PPV material. Each layer deposited in this manner gives a thickness of the order of 10nm. Such thicknesses are about ten times thinner than the thinnest layers which could be applied using prior art methods.

The PPV precursor may be cured using conventional methods, e.g. by heating in an oven with a controlled atmosphere of nitrogen.

Subsequently, a top electrode of aluminium [11] may be deposited on the printed active layer by standard processes such as spinning, thermal evaporation or sputtering or the electrode may be printed on in a similar manner to that used for applying the PPV layer. Additional layers such as conductive polymers [12], charge-trapping or charge-diffusion layers [13] between the active layer and the conductive layers, or barrier films [14] surrounding the device can be employed to enhance efficiency, reduce power requirements or increase lifetime. Suitable completed structures may be as shown in Figures 2 and 3.

Suitable operating voltages for such EL devices start as low as 5V.

Although the invention has been described using the particular embodiment of offset lithographic printing, it is not intended that the claims should be limited by this. Given the teaching of this document and thus overcoming the present technical prejudices to come to the realisation that LEPs can be printed using a standard printing technique, a person skilled in the

art would appreciate that any other printing process would also work including, though not limited to letter-press printing, screen-printing, doctor blade coating, roller printing, reverse-roller printing, offset lithographic printing, flexographic printing and web offset printing.

Also, although Light Emitting Polymers have been described with reference to a particular class of conjugated polymers such as poly(p-phenylenevinylene) (PPV), it is not intended 10 that the claims should be limited by this. Light Emitting Polymer is used as a term to describes materials consisting of a single substance and having electroluminescent characteristics.

15 Having overcome the technical prejudices, the present invention leads to the ability to produce large quantities of accurately formed electroluminescent devices at very low cost. Such an ability can potentially drastically change the whole area of display technology. It would now be possible to 20 produce low cost, disposable, flat TV and computer screens as well as extending the possible areas of application of electroluminescent displays to such areas as packaging, moving picture instruction labels, business cards, magazine covers, identity cards, menus, anticounterfeiting devices, etc.

Claims

1. A method of producing an electroluminescent device which comprises the steps of:
  - 5 -applying a first conductive electrode to a substrate;
  - using a standard printing process to apply a Light Emitting Polymer on top of though not necessarily adjacent to said first electrode;
  - 10 - applying a second conductive electrode on top of though not necessarily adjacent to said Light Emitting Polymer;
  - 15 whereby an accurately-placed layer of Light Emitting Polymer of controllable thickness is formed using a method which is as fast and cost-effective as desired.
- 20 2. A method of producing an electroluminescent device according to claim 1 wherein said process is selected from the group consisting of letter-press printing and screen-printing and doctor blade coating and ink-jet printing.
- 25 3. A method of producing an electroluminescent device according to claim 1 wherein said process is selected from the group consisting of roller printing and reverse-roller printing and offset lithographic printing and flexographic printing and web printing.
- 30 4.. A method of producing an electroluminescent device according to any of the preceding claims wherein said Light Emitting Polymer is mixed with a polar solvent.
- 35 5. A method of producing an electroluminescent device according to claim 4 wherein said polar solvent is an aqueous solution.

6. A method of producing an electroluminescent device according to any of the preceding claims wherein said standard printing process is carried out in a controlled atmosphere.

5

7. A method of producing an electroluminescent device according to any of the preceding claims wherein the viscosity and evaporation of the Light Emitting Polymer solution is controlled by controlling the temperature of a stage of the standard printing process.

10

8. A method of producing an electroluminescent device according to any of claims 3 to 7 wherein the temperature is controlled by controlling the temperature of the printing rollers.

15

9. A method of producing an electroluminescent device according to any of the preceding claims which comprises the extra step of applying barrier layers to any of the applied layers.

20

10. A method of producing an electroluminescent device according to any of the preceding claims which comprises the extra step(s) of applying additional charge trapping or charge diffusion layers between any of said first conductive electrode, layer of Light Emitting Polymer and second conductive electrode.

25

# INTERNATIONAL SEARCH REPORT

Int'l. Application No  
PCT/GB 98/02211

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 H05B33/10

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 85 03596 A (ROGERS CORP) 15 August 1985 see the whole document -----	1,2,4,7
X	DATABASE WPI Section Ch, Week 9203 Derwent Publications Ltd., London, GB; Class L03, AN 92-020645 XP002080741 & JP 03 269995 A (RICOH KK) , 2 December 1991 see abstract -----	1,2
A,P	WO 98 30069 A (E L SPECIALISTS INC) 9 July 1998 see the whole document -----	1,2,9,10

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

14 October 1998

Date of mailing of the international search report

22/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Drouot, M-C

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 98/02211

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 8503596	A 15-08-1985	CA	1227522 A	29-09-1987
		EP	0171420 A	19-02-1986
		JP	7066855 B	19-07-1995
		JP	61501177 T	12-06-1986
		US	4832459 A	23-05-1989
		US	4816717 A	28-03-1989
WO 9830069	A 09-07-1998	AU	5724398 A	31-07-1998